Notes for the Practical Problems:

In the practical preparatory problems we have not included specific details of handling or disposal of labaratory materials and wast as regulations vary greatly from country to country.

We take it for granted that the students are able to perform basic experimental techniques such as titration, filtration, recrystallisation, distillation.

As mentioned in the preface we attach great importance to safety.
The rules below have to be followed during laboratory work at the 36th IChO in Kiel.

- The students have to bring their own labaratory coats.
- When the students enter the labs they must familiarise themselves with the locations of
  emergency exits
  safety shower, fire blanket and eye wash.
- Laboratory coats, eye protections and closed shoes must be worn at all times in the laboratories. Long hair has to be tied.
- Coats and bags are forbidden in the laboratory. They have to be deposited in the cloakroom.
- Eating, drinking or smoking in the laboratory or tasting any chemicals are strictly forbidden.
- Pipetting by mouth is strictly forbidden.
- All potentially dangerous materials will be labelled by international symbols. Each student is responsible for recognizing these symbols and knowing their meaning.
- Do not dispose of chemicals down the sink. Follow all disposal rules provided by the organizer.
- Do not hesitate to ask an instructor if you have any questions concerning safety issues.

A brief instruction will be given on the day preceding the examination.

Apologies for all the do’s and don’t’s - we guarantee that the students will still be allowed to perform the experiments and we hope they will enjoy it!

Problem 35: Preparation and volumetric determination of strontium peroxide octahydrate

Introduction

Peroxo compounds play an important role in many areas including e. g. perborates or percarbonates in the detergent industry or peroxo compounds for the whitening of a variety of products.

Barium peroxide is one of the best-known peroxides. It can be prepared by the oxidation of barium oxide with oxygen in a reversible reaction. However, the peroxide content of BaO_2 is always lower than that calculated.

$$2\ BaO + O_2 \underset{700\ °C}{\overset{500\ °C}{\rightleftharpoons}} 2\ BaO_2$$

Because of the reversibility of this reaction, barium peroxide provides a means of storage of elemental oxygen and several years ago, it was the only source of oxygen gas.

The peroxide content of such compounds can be determined by reaction with an excess of acid to give dihydrogen peroxide followed by a titration with a standard solution of potassium permanganate. This quantitative method is widely used in all areas where peroxides are of importance.

This practical exercise involves the preparation of strontium peroxide, determinimation of the strontium content by a complexometric titration and determination of the peroxide content by manganometric analysis.

List of chemicals

reagent	**concentration**	**R phrases**	**S phrases**
ammonia	$w(NH_3)$ = 25 %	34-50	26-36/37/39-45-61
EDTA disodium salt	$c(Na_2EDTA) = 0.1\ mol\ L^{-1}$		
ethanol	$w(C_2H_5OH)$ = 96 %	11	7-16
hydrogen peroxide	$w(H_2O_2)$ = 3%	34	3-26-36/37/39-45
methyl red	solid		
naphthol green B	solid		
perchloric acid	$w(HClO_4)$ = 10%	10-35	23.2-26-36/37/39-45
phthalein purple	solid		
potassium permanganate	$c(KMnO_4) = 0.1\ mol\ L^{-1}$		
strontium chloride hexahydrate	solid		

Procedure 1: Preparation of strontium peroxide

5.0 g of strontium chloride hexahydrate are dissolved in about 2.5 mL of distilled water and 25 mL of dihydrogen peroxide ($w(H_2O_2)$ = 3%) are added. A solution of 3.5 mL of ammonia ($w(NH_3)$ = 25%) in 50 mL of distilled water is added to the mixture to give strontium peroxide octahydrate on standing. The precipitate is filtered off, and dried at about 150°C. In this procedure, the octahydrate transforms nearly completely into the anhydrous compound. An extremely small amount of water remains in the product and the peroxide content is slightly lower than calculated for SrO_2. At higher temperatures, strontium peroxide decomposes rapidly. Note: calcium peroxide can be prepared similarly.

Record the yield of the product in g.

Procedure 2: Manganometric determination of the peroxide content

About 100 mg of the product prepared in procedure 1 (record the exact weight) are transferred into a 300 mL Erlenmeyer flask and the contents dissolved in 5 mL of perchloric acid. The volume of the solution is increased to about 100 mL by addition of water. The determination of the peroxide content is performed by titration with potassium permanganate solution ($c(KMnO_4) = 0.02\ mol \cdot L^{-1}$), until the solution is slightly pink in colour. At the beginning, the solution has to be titrated slowly because of the slow rate of reaction. The latter can be accelerated by the addition of a small amount of a manganese(II) compound.

Record the volume of the potassium permanganate solution used in the titration in mL.

Procedure 3: Complexometric determination of the strontium content

About 100 mg of the product prepared in procedure 1 (record the exact weight) are transformed into a 300 mL Erlenmeyer flask and the contents dissolved in 5 mL of perchloric acid. The solution is made up to a volume of 50 mL and 15 mL of ammonia solution, 60 mL of ethanol and 2 mL of phthalein purple indicator are added. The resulting deep purple solution is titrated with disodium EDTA ($c(Na_2EDTA) = 0.1\ mol\ L^{-1}$) until the solution is intense light-green in colour.

Record the volume of the Na_2EDTA solution in mL

Preparation of the phthalein purple indicator

100 mg of phthalein purple, 5 mg of methyl red and 50 mg of naphthol green B are dissolved in 2 mL of ammonia solution. The solution is filled up to a volume of 100 mL. The indicator is stable for up to a period of one week.

35.1 Calculate the yield (%) of the product based on the theoretical yield of strontium chloride hexahydrate.

35.2 Calculate the content of the liberated dihydrogen peroxide in percent for the manganometric analysis and compare this value with the theoretical value of SrO_2.

35.3 Calculate the strontium peroxide content in percent determined by the manganometric analysis.

35.4 Calculate the strontium peroxide content in percent determined by the complexometric determination

35.5 Write down the equation of the formation of SrO_2 from $SrCl_2$, H_2O_2 and NH_3.

35.6 Write down the equation for the reaction of permanganate anions with dihydrogen peroxide in an acidic solution

35.7 Why will the reaction in the manganometric analysis proceed faster if a manganese(II) salt is added to the mixture?

Problem 36: Preparation and iodometric determination of potassium iodate

Introduction

Iodometric analysis is one of the most important volumetric procedures, because concentrations of both oxidizing and reducing agents, can be accurately determined using this approach. The reaction between thiosulfate dianions and elemental iodine in a neutral or acidic solution is the basis of this method.

$$2\,S_2O_3^{2-} + I_2 \rightleftharpoons S_4O_6^{2-} + 2\,I^-$$

blue colourless

For the determination of oxidizing agents an excess of potassium iodide and a small amount of an acid are added to the sample solution. The iodine formed in this reaction is titrated with sodium thiosulfate solution.

In contrast a back titration is typically performed for the determination of reducing agents in which a well defined excess of an iodine solution is added to the sample solution and the unreacted iodine is titrated with thiosulfate solution. Potassium iodate is used as a titrimetric standard for the standardization of the thiosulfate solution, because of its high stability and the fact that it can be produced in a very pure state. If an excess of potassium iodide is added to a well defined amount of potassium iodate in an acidic solution, an equivalent amount of iodine will be generated which can be titrated with sodium thiosulfate solution.

The practical exercise involves the preparation of potassium iodate and the determination of its purity by iodometric titration.

List of chemicals

reagent	**concentration**	**R phrases**	**S phrases**
acetic acid	w(H_3CCOOH) = 5%		
ethanol	w(C_2H_5OH) = 96 %	11	7-16
hydrochloric acid	c(HCl) = 2 mol L^{-1}	34	26-36/37/39-45
potassium iodide	solid	63-36/38-42/43	26-36/37/39-45
potassium permanganate	solid	8-22	2
sodium thiosulfate	c($Na_2S_2O_3$) = 0.1 mol L^{-1}		

Procedure 1: Preparation of potassium iodate

6 g of potassium permanganate are dissolved in 150 mL of hot distilled water. 3 g of potassium iodide dissolved in a small amount of distilled water are added to the solution.

The reaction mixture is heated on a boiling water bath for 30 min. The unreacted potassium permanganate is removed by the addition of ethanol. During this procedure, the supernatant liquid becomes colourless.

The resulting precipitate of manganese(IV) oxide is filtered off and the filtrate is acidified by the addition of acetic acid. The solution is concentrated by heating on a water bath until the product begins to crystallize. The solution is allowed to cool to room temperature. The crystalline product is filtered off and washed with a small amount of ethanol. More product can be isolated by further concentration of the mother liquor. The product can be recrystallized from water and dried at 110°C.

Record the yield of the product in g

Procedure 2: Iodometric determination of the purity of the isolated potassium iodate.

If a 25 mL burette is to be used in the determination take about 60 mg of the product prepared in procedure 1 (record the exact weight) and dissolve it in about 100 ml of distilled water. Add 1 g of potassium iodide to the solution and slightly acidify with dilute hydrochloric acid. The solution is titrated with sodium thiosulfate solution (c($Na_2S_2O_3$) = 0.1 mol L^{-1}) until it

becomes colourless. Just before the end point 2 - 3 mL of starch solution are added as an indicator.
Record the volume of the sodium thiosulfate solution used in mL

Preparation of the starch solution:
About 2 g of starch are suspended in 3 mL of distilled water and the suspension vigorously stirred. The mixture is added to 300 mL of boiling water and heated for about two min. Any undissolve starch should be removed by decanting.
The starch solution should be prepared as required, however, it can be kept for a longer period by the addition of a small amount of a mercury(II) iodide solution.

36.1 Calculate the yield (%) of the product.

36.2 Calculate the purity of your product in a percentage.

36.3 Give the equation for the reaction between iodate and iodide anions in an acidic solution.

36.4 What name is given to the redox reaction in 36.3?

36.5 Why should an iodometric determination not be performed in an alkaline solution ?

36.6 What is the expected trend in oxidising ability on going from fluorine to iodine? Givew the explanation for this trend.

36.7 How can the following ions be determined iodometrically? In each case give the appropriate equation:
a) iron(III) cations
b) copper(II) cations
c) sulfide anions

Problem 37: Qualitative analysis of anions in an unknown mixture

Introduction
Besides the quantitative analysis of chemical compounds, the qualitative analysis of unknown substances or mixtures of substances in order to identify the cations and/or anions is also an important procedure in analytical chemistry.
Cations have to be seperated prior to identification, however, this is not the case for anions.
In this exercise, the anions in an analytical sample are to be identified. Some of these anions can be identified by direct analysis of the solid sample, however, for other it is necessary to identify them in the filtrate of a soda extract. Several reagents are provided that can either be used in the initial identification of the anions present, or to perform the necessary confirmation tests for a particular anion.
The reactions of the anions with the reagents that are available, as far as is necessary for your analysis, are described below.

List of potential anions:
acetate H_3CCOO^-
carbonate CO_3^{2-}
chloride Cl^-
chromate CrO_4^{2-}
nitrate NO_3^-
oxalate $C_2O_4^{2-}$
perchlorate ClO_4^-
sulfate SO_4^{2-}

Preparation of the soda extract

One spatulaful of the sample (about 1 g) is mixed with 2 – 3 times the amount of sodium carbonate. The mixture is suspended in water and heated for 10 minutes. After cooling, the residue is filtered off and washed with water. The filtrate is used in the anion identification. It is always a good idea to use blind samples for comparison and to check the purity of soda.

Selected reactions of the anions that may be present:

Acetate

Theory: Acetate anions react with potassium hydrogensulfate to form acetic acid:

$$H_3CCOO^- + HSO_4^- \longrightarrow H_3CCOOH + SO_4^{2-}$$

Dilute sulfuric acid also forms acetic acid upon reaction with acetate anions.

Procedure: The solid sample is grinded with four times the amount of potassium hydrogensulfate in a mortar. In the presence of acetate anions, there is the characteristic smell of acetic acid.

Carbonate

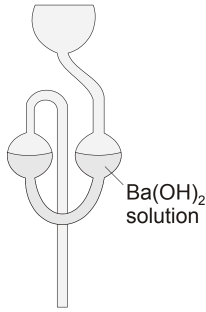
Theory: Carbonate anions react with dilute hydrochloric acid to form unstable carbonic acid that decomposes into water and carbon dioxide:

$$CO_3^{2-} + 2\,H^+ \longrightarrow \{H_2CO_3\} \longrightarrow CO_2\uparrow + H_2O$$

Carbon dioxide reacts with barium hydroxide to form barium carbonate:

$$CO_2 + Ba(OH)_2 \longrightarrow BaCO_3 + H_2O$$

Procedure: In a test tube, dilute hydrochloric acid is added to a small amount of the sample. The test tube is closed immediately connected to a fermentation tube filled with freshly prepared barium hydroxide solution. The test tube is gently heated. In the presence of carbonate anions, white flakes of barium carbonate are observed in the solution in the fermentation tube within 3 - 5 minutes.



schematic representation of a fermentation tube

Chloride

Theory: Chloride anions in a nitric acid solution react with silver nitrate to form silver chloride:

$$Ag^+ + Cl^- \longrightarrow AgCl$$

Silver chloride is soluble in concentrated ammonia solution. It is insoluble in concentrated nitric acid.

Procedure: An aqueous solution of silver nitrate is added to 5 mL of the soda extract acidified with dilute nitric acid. In the presence of chloride anions, white silver chloride precipitates from solution. The latter decomposes into elementary silver within a few hours if it is exposed to sunlight.

Chromate

Theory: Chromate anions react with silver nitrate in a neutral or dilute nitric acid solution to form silver chromate:

$$2\ Ag^+ + CrO_4^{2-} \longrightarrow Ag_2CrO_4$$

Silver chromate is soluble in acids and ammonia solution.

Procedure: An aqueous solution of silver nitrate is added to 5 mL of the soda extract that is acidified with dilute nitric acid. In the presence of chromate anions, reddish brown silver chromate precipitates from the solution.

Theory: Chromate anions react with barium chloride in an acetic acid solution buffered by ammonium acetate to form barium chromate:

$$Ba^{2+} + CrO_4^{2-} \longrightarrow BaCrO_4$$

Barium chromate is soluble in strong mineral acids.

Procedure: A spatulaful of ammonium acetate is added to 5 mL of the soda extract that has been acidified with acetic acid. An aqueous solution of barium chloride is added and the mixture boiled for 2 minutes. In the presence of chromate anions, yellow barium chromate precipitates from the solution.

Concentrated, yellow coloured, chromate containing solutions form orange coloured dichromates upon acidification with dilute sulfuric acid. The addition of more highly concentrated sulfuric acid leads to the formation of dark coloured oligo- and polychromates.

Nitrate

Theory: Nitrate anions are reduced to nitrogen monoxide (NO) by iron(II) sulfate in solutions acidified with sulfuric acid. Nitrogen monoxide reacts with iron(II) cations to form the brownish nitrosyl complex $[Fe(NO)(H_2O)_5]^{2+}$.

Procedure: 2.5 mL of an iron(II) sulfate solution acidified with sulfuric acid is added to 2.5 mL of the soda extract. After mixing, the test tube is brought into a skew position and concentrated sulfuric acid is poured carefully along the inner surface. In the presence of nitrate anions, a brownish ring forms at the phase boundary between the soluton and the sulfuric acid.

Oxalate

Theory: In a neutral solution, oxalate anions react with silver nitrate solution to form silver oxalate:

$$2\ Ag^+ + C_2O_4^{2-} \longrightarrow Ag_2C_2O_4$$

Silver oxalate is sparingly soluble in acetic acid. It is soluble in nitric acid and ammonia solution.

Procedure: An aqueous solution of silver nitrate is added to 5 mL of the soda extract neutralized with acetic acid. In the presence of oxalate anions, a white precipitate of silver oxalate is formed.

Theory: Oxalate anions react in an ammoniacal or acetic acid solution that is buffered by sodium acetate, with calcium chloride to form calcium oxalate:

$$Ca^{2+} + C_2O_4^{2-} \longrightarrow CaC_2O_4$$

Calcium oxalate is insoluble in dilute acetic acid. It is soluble in strong mineral acids. Calcium oxalate is oxidized to carbon dioxide by potassium permanganate in an acidic solution. In this reaction, the manganese(VII) cations are reduced to manganese(II) cations.

Oxalates and oxalic acid decompose by reaction with concentrated sulfuric acid into carbon monoxide and carbon dioxide:

$$H_2C_2O_4 \xrightarrow{H_2SO_4} H_2O + CO\uparrow + CO_2\uparrow$$

Procedure: 5 mL of the soda extract are acidified with acetic acid. Ammonia solution is added until the mixture is slightly ammoniacal followed by the addition of an aqueous solution of calcium chloride. In the presence of oxalate anions, white calcium oxalate precipitates from solution. The precipitate is filtered off and dissolved in sulfuric acid. A solution of potassium permanganate is added dropwise to the solution. The potassium permanganate solution rapidly decolourizes and a gas is formed.

Theory: In a neutral solution, oxalate anions react with barium chloride to form barium oxalate:

$$Ba^{2+} + C_2O_4^{2-} \longrightarrow BaC_2O_4$$

Barium oxalate dissolves in dilute acetic acid.

Procedure: An aqueous solution of barium chloride is added to 5 mL of the soda extract neutralized with dilute hydrochloric acid. In the presence of oxalate anions, white barium oxalate precipitates from the solution.

Perchlorate

Theory: In a solution slightly acidified with nitric acid, perchlorate anions react with potassium nitrate to form potassium perchlorate:

$$ClO_4^- + K^+ \longrightarrow KClO_4$$

Potassium perchlorate is insoluble in cold water and cold dilute acid.

Procedure: An aqueous solution of potassium nitrate is added to 5 mL of the soda extract slightly acidified with nitric acid. In the presence of perchlorate anions, a white precipitate of potassium perchlorate forms.

Theory: In a neutral and slightly alkaline solution perchlorate anions are reduced by iron(II) hydroxide (formed by the reaction of iron(II) sulfate with sodium hydroxide) to chloride anions.

Procedure: 4 mL of an aqueous iron(II) sulfate solution are added to 5 mL of the soda extract acidified with dilute nitric acid. Dilute sodium hydroxide solution is added until some iron(II) hydroxide begins to precipitate from solution or the solution is slightly alkaline. The mixture is boiled for a few minutes and the resulting precipitate is filtered off. In the presence of perchlorate anions, the filtrate of the reaction contains chloride anions, which can be confirmed by reaction with silver nitrate in a solution acidified with nitric acid .

Sulfate

Theory: In an acidic solution acidified with hydrochloric acid sulfate anions react with barium chloride to form barium sulfate:

$$Ba^{2+} + SO_4^{2-} \longrightarrow BaSO_4$$

Barium sulfate is insoluble in concentrated hydrochloric acid and in concentrated nitric acid. It is sparingly soluble in hot concentrated sulfuric acid, 12 percent of barium sulfate dissolves.
Procedure: An aqueous solution of barium chloride is added to 5 mL of the soda extract acidified with dilute hydrochloric acid. In the presence of sulfate anions white barium sulfate precipitates from the solution.

Theory: In an acidic solution acidified with hydrochloric acid, sulfate anions react with calcium chloride to form calcium sulfate:

$$Ca^{2+} + SO_4^{2-} \longrightarrow CaSO_4$$

Calcium sulfate dissolves in concentrated sulfuric acid and concentrated hydrochloric acid.
Procedure: An aqueous solution of calcium chloride is added to 5 mL of the soda extract acidified with dilute hydrochloric acid. In the presence of sulfate anions, white calcium sulfate precipitates from the solution. The precipitation is not quantitative!

37.1 Which anions are present in your sample?

37.2 Give the equations of the reaction of nitrate anions with iron(II) cations and of the subsequent formation of the nitrosyl complex.

37.3 Why does the brownish coloured complex form directly at the phase boundary between the solution and concentrated sulfuric acid?

37.4 Write the equation of the reaction of permanganate anions with oxalate anions in an acidic solution.

37.5 Write the equation of the reaction of perchlorate anions with iron(II) hydroxide in a neutral solution.

List of chemicals

reagent	**concentration**	**R phrases**	**S phrases**
acetic acid	w(H_3CCOOH) = 99%	10-35	23-26-45
acetic acid	w(H_3CCOOH) = 5%		
ammonia	w(NH_3) = 25%	34-50	26-36/37/39-45-61
ammonium acetate	solid		
barium chloride	c($BaCl_2 \cdot 2\ H_2O$) ~ 1.5 mol L^{-1}	20/22	28
barium hydroxide	w($Ba(OH)_2 \cdot 8\ H_2O$) ~ 2 %	20/22-34	26-36/37/39-45
calcium chloride	c($CaCl_2 \cdot 2\ H_2O$) = 1 mol L^{-1}	36	22-24
hydrochloric acid	w(HCl) = 36%	34-37	26-45
hydrochloric acid	c(HCl) = 2 mol L^{-1}	34	26-36/37/39-45
iron(II) sulfate	c($FeSO_4 \cdot 7\ H_2O$) = 1 mol L^{-1}	22	24/25
nitric acid	w (HNO_3) = 65%	8-35	23-26-36-45
nitric acid	c (HNO_3) = 2 mol L^{-1}	8-35	23-26-36-45
potassium hydrogensulfate	solid	34-37	26-36/37/39-45
potassium nitrate	saturated	36/38	26
potassium permanganate	c($KMnO_4$) = 0.02 mol L^{-1}	52/53	61
silver nitrate	c($AgNO_3$) = 0.2 mol L^{-1}	34-51/53	26-36/37/39-45-61
sodium acetate	solid		

sodium carbonate	solid	36	22-26
sodium hydroxide	w(NaOH) ~ 5 %	35	26-37/39-45
sulfuric acid	w(H_2SO_4) = 95-97 %	35	26-30-45
sulfuric acid	c(H_2SO_4) = 2 mol L^{-1}	35	26-30-45

Preparation of the sample:

To avoid interferences in the qualitative determinations only certain selected counter ions should be present in the analytical sample. The following salts guarantee the determination of anions without any interference: LiCl, $LiClO_4$, $Na(OOCCH_3)$, Na_2CO_3, NaCl, $NaNO_3$, $Na_2C_2O_4$, $NaClO_4$, Na_2SO_4, K_2CO_3, $K_2Cr_2O_7$, KNO_3, K_2SO_4, $AlCl_3$, $Al_2(SO_4)_3$, $FeCl_2$, $FeSO_4$, $CoCl_2$, $Co(NO_3)_2$, $CoSO_4$, $NiCl_2$, $Ni(NO_3)_2$, $NiSO_4$. Certain other salts can be used. The salts must not form sparingly soluble residues. If salts are to be used that are not mentioned in the following table, then the hazard and safety data sheets for the compounds must first be consulted.

salt	**formula**	**R phrases**	**S phrases**
aluminium chloride	$AlCl_3 \cdot 6\ H_2O$	36/38	
aluminium sulfate	$Al_2(SO_4)_3 \cdot x\ H_2O$		24/25
cobalt(II) chloride	$CoCl_2 \cdot 6\ H_2O$	49-22-42/43-50/53	53-22-45-60-61
cobalt(II) nitrate	$Co(NO_3)_2 \cdot 6\ H_2O$	22-20-43	36/37
cobalt(II) sulfate	$CoSO_4 \cdot 7\ H_2O$	49-22-42/43-50/53	53-22-45-60-61
iron(II) chloride	$FeCl_2 \cdot 4\ H_2O$	22-38-41	26-39
iron(II) sulfate	$FeSO_4 \cdot 7\ H_2O$	22	24/25
lithium chloride	LiCl	22-36/38	
lithium perchlorate	$LiClO_4$	8-22-36/37/38	17-26-36
nickel(II) chloride	$NiCl_2 \cdot 6\ H_2O$	25-43-50/53	24-37-45-61
nickel(II) nitrate	$Ni(NO_3)_2 \cdot 6\ H_2O$	8-22-43	24-37
nickel(II) sulfate	$NiSO_4 \cdot 6\ H_2O$	22-40-42/43-50/53	22-36/37-60-61
potassium carbonate	K_2CO_3	36/37/38	22-26
potassium dichromate	$K_2Cr_2O_7$	49-46-21-25-26-37/38-41-43-50/53	53-45-60-61
potassium nitrate	KNO_3	36/38	26
potassium sulfate	K_2SO_4		
sodium acetate	NaH_3CCOO		
sodium carbonate	Na_2CO_3	36	22-26
sodium chloride	NaCl		
sodium nitrate	$NaNO_3$	8-22-36	22-24-41
sodium oxalate	$Na_2C_2O_4$	21/22	24/25
sodium perchlorate	$NaClO_4 \cdot H_2O$	9-22	13-22-27
sodium sulfate	Na_2SO_4		